Natural Environment Research Council

Institute of Geological Sciences

Mineral Reconnaissance Programme Report

A report prepared for the Department of Industry

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No. 52

Miscellaneous investigations on mineralisation in sedimentary rocks

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Report No. 52

Geochemical reconnaissance in the Cheshire Basin

J. H. Bateson

CONTENTS

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SUMMARY

Five areas on the outcrop of the Helsby Sandstone Formation (formerly Keuper Sandstone) and Tarporley Siltstone (formerly Waterstone) (Warrington and others, 1980) coinciding with known mineralisation were selected as targets for a geochemical investigation. About 3750 soil samples were collected and analysed for copper, lead, cobalt and nickel. Geochemical maps are presented to show the occurrence and distribution of anomalous values.

In all the five areas investigated the geochemistry of the soils identified the known areas of mineralisation. In several instances other small areas were also indicated where the soil values are anomalously high and are presumed to reflect local, hitherto unknown, mineralisation. None of these areas, however, appear to have the areal extent necessary for economic deposits.

The results of this preliminary investigation indicate that in all cases the mineralisation is very closely associated with permeable and porous sandstone units which are faulted against less permeable units forming trap structures for migrating mineralising fluids.

INTRODUCTION

The areas described in this report are located at the outcrop of the Helsby Sandstone Formation (Keuper Sandstone) in two regions on the periphery of the Cheshire Basin. The investigations were undertaken at the north-eastern outcrop near Alderley Edge and in the extreme south around Wem and Ruyton (Figure 1).

Physiographically the Cheshire Basin is an area of low-lying undulating terrain with a surrounding discontinuous rim of low ridges and hills which coincide with the outcrop of the more resistant Helsby Sandstone (Hull and Green, 1866; Pocock and Wray, 1925; Taylor and others, 1963; Poole and Whiteman, 1966). With the exception of the ridges and hills, the area is mantled by a thick and continuous sheet of boulder clay and glacial outwash deposits. Knowledge of the solid geology in these areas is derived almost exclusively from borehole data.

At a number of localities copper ore has been found in the sedimentary succession of the Triassic, most frequently in the basal sandstones and conglomerates of the Helsby Sandstone Formation. The ore usually occurs in the form of carbonates in the cement of the sandstones. Cobalt, lead and vanadium are also recorded from some of the mines. There is a continuing debate regarding the origin of the ore minerals and the function of the faults frequently associated with the known deposits. The principal mines were at Alderley Edge, Mottram St Andrew (Kirkleyditch), Eardiston and Grinshill.

Soil samples were collected on regular grid traverses from five separate areas over the outcrop of the Helsby Sandstone Formation. Each of the areas was selected to include known occurrences of mineralisation. All the samples were analysed for copper and lead, with cobalt and nickel determined in selected samples.

GEOCHEMICAL INVESTIGATIONS

The geochemical investigations were undertaken to examine the applicability of the soil-sampling technique and in an attempt to identify extensions to the known mineralisation.

As there were well-defined areas of interest, the investigations were restricted to soil sampling on regular grids. Local conditions and the overall size of area determined the spacing of samples, which varied from 100 X 100 m to 250 X 100 m, giving sample densities between 120 and 55 samples per km^2. The soil samples were taken with a hand auger from the B horizon – usually found to be 45–60 cm from surface. Soil thickness was found to vary between one area and another; the soil cover was generally relatively thin on the hilly ground, but was much thicker on the till-covered lower lying areas. In the Alderley Edge investigation the degree of variability in the amount of soil/till overlying the bedrock within the area was so large that it was necessary to treat the soil samples as two distinct populations, one population from areas of relatively thin cover and the other derived from the drift-covered plain.

All samples after drying and sieving were analysed by atomic absorption spectrophotometry for Cu, Pb, Co and Ni and the data plotted on suitable maps to demonstrate the extent of areas of anomalous values.

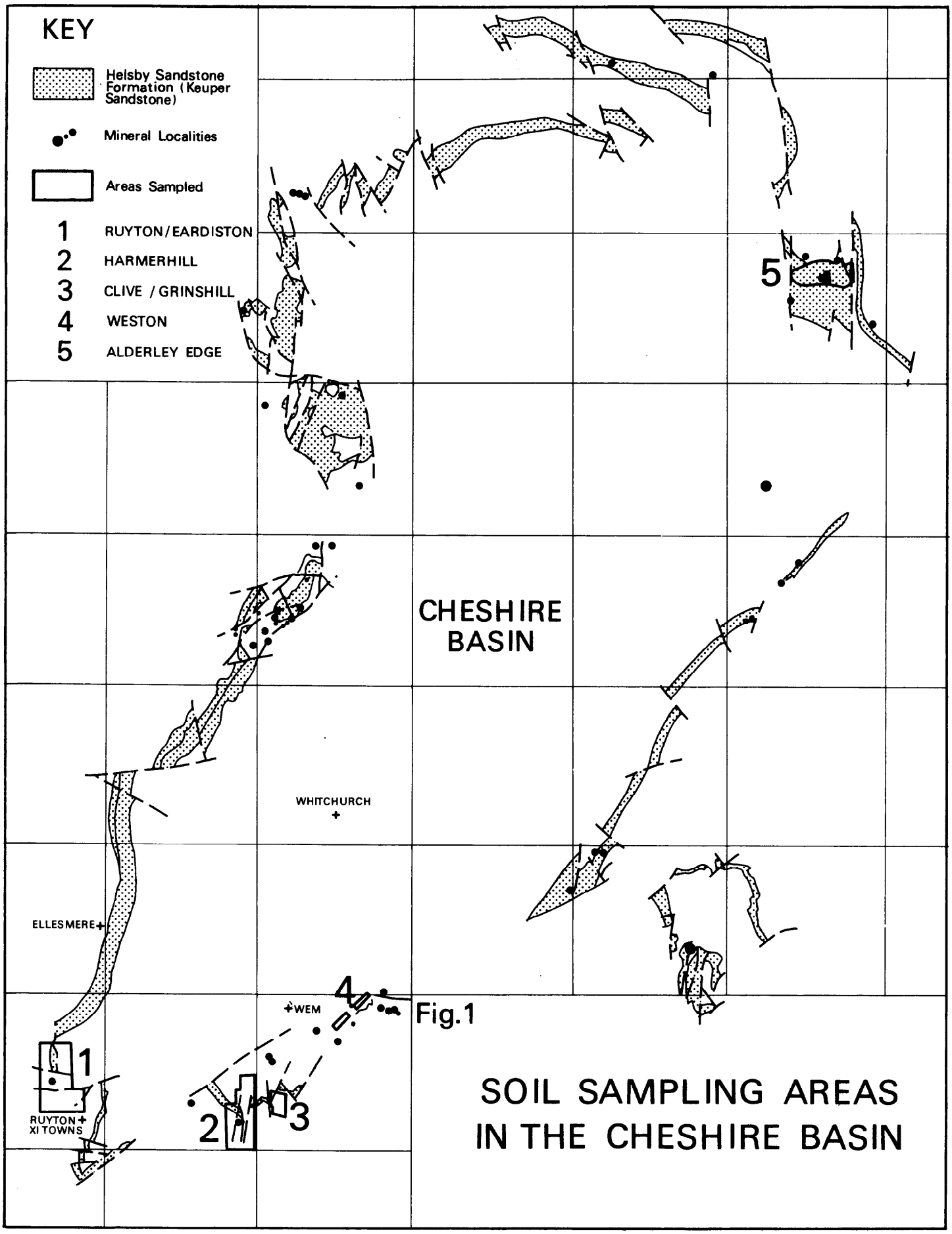

Fig.1

SOIL SAMPLING AREAS IN THE CHESHIRE BASIN

AREA 1: RUYTON–EARDISTON

The area of this investigation (Figure 2) lies some 10 km to the south of Ellesmere, occupying an area of 10 km^2 where the Helsby Sandstone and the highest beds of the underlying Wilmslow Sandstone Formation (Upper Mottled Sandstone) crop out on the shallow dipping western flank of the Cheshire Basin. These sandstones, known locally as the Ruyton Sandstone consist of a group of red and yellow freestones overlying the middle and lower beds of the Wilmslow Sandstone Formation (Upper Mottled Sandstone). At outcrop they form an arcuate line of low hills rising to a little in excess of 130 m in contrast to the lower undulating terrain both to the west and to the east where the Mercia Mudstones (Keuper Marls) form the low-lying plain at an altitude of a little over 100 m.

All of the area, with the exception of the hills referred to above, is covered by glacial material of variable thickness consisting of boulder clay with lenses of poorly sorted sands and gravels.

Faults in the area can be demonstrated by the displacement of the various lithologies, and generally trend in roughly east-west and north-south directions. One of these faults, trending NNE, extending south-westwards from Eardiston to Elbridge, is known to be associated with mineralisation and during the early 19th century supported a small mine. The ore, predominately malachite, occurs not only along the fault plane but also in the wall rock. The mineralised zone is said to average about 1.25 m in width but varies from a few centimetres to 1.56 m (Dewey and Eastwood, 1925). According to Henwood (quoted *in* Dewey and Eastwood, 1925) the lateral extent of the mineralisation is restricted by the occurrence of a layer of blue clay. The available evidence suggests that the mineralisation is concentrated in the Ruyton Sandstone where faulting throws it against the more impervious Tarporley Siltstones. Upward migrating metalliferous fluids in the Ruyton Sandstone would be impeded by the clays and siltstones (Carlon, 1981).

Geochemical investigation

Soil samples were taken and analysed from a 130 X 100 m grid laid out so that the traverse lines were approximately normal to the strike of the rocks. Figure 2 shows the distribution of samples containing anomalous copper or cobalt. Only a small proportion of the samples were analysed for lead; those that have anomalous values do not produce an interpretable pattern and are not shown on Figure 2.

The analytical data were subjected to simple statistical computations in order to establish the threshold value, taken at the mean plus two standard deviations ($\bar{x} + 2\sigma$). In order to reduce the 'weighting' effect of very high values, the highest values (amounting to approximately 2.5% of the population) were rejected before calculating the mean and standard deviations. The data are presented below; all values are recorded in ppm.

	n	$\bar{x}$	σ	Rejection limit	Range	$\bar{x} + 2\sigma$
Copper	1475	20.19	15.48	50	5–1540	51.15
Cobalt	1475	10.53	3.58	20	0–40	17.69
Lead	180	35.9	11.86	90	20–180	59.62

The distribution of the anomalous values is indicated in Figure 2 in relation to the main features of the geology. The maximum concentration of copper values occurs in the vicinity of the fault which extends from Eardiston to Elbridge on which the disused Eardiston Mine is situated. Dispersal of high values away from the fault extends for a distance of some 300 m downslope from the fault at surface. At a distance of about 400 m north of the village of Eardiston, at Tedsmore, there is another small group of high value copper samples which probably represent dispersal from minor mineralisation associated with the north-eastward extension of the mineralised fault at Eardiston Mine.

The anomalous cobalt values show a much wider dispersal pattern than the high copper values, extending up to 1 km from the site of the old mine.

It is of interest to note that there are very few anomalous cobalt values to the west of the known mineralised zone. This is probably related partly to the fairly high mobility of cobalt, and partly to the eastwards migration of the Welsh Ice. On the basis of present evidence it is thought likely that the group of high values to the north of Park Cottages (near to Park House) represents dispersed values rather than concealed mineralisation.

AREA 2: HARMERHILL

An area of approximately 7.5 km^2 was sampled on a 100 X 100 m grid, and the soils were analysed for Cu, Pb and Co. The area investigated (Figure 3) straddles the Shotton Hall Fault and a similar parallel fault structure which passes through Pim Hill some 500–600 m to the west. Here the Ruyton Sandstone and Tarporley Siltstones (Waterstones) form topographic highs (rising to 163 m at Pim Hill) above the surrounding lower-lying country, overlain by the Mercia Mudstones to the east and underlain by the softer Wilmslow Sandstone (Upper Mottled Sandtone) in the west. The lower areas are overlain by a variable thickness of glacial material comprising chiefly boulder clay with irregular intercalations of sand and gravel.

The two main faults extend approximately northwards through the area and both are known to be mineralised intermittently along strike. The most westerly, at Pim Hill, downthrows the lower part of the Helsby Sandstone against the Wilmslow Sandstone. Along the line of this fault copper, cobalt and some vanadium have been

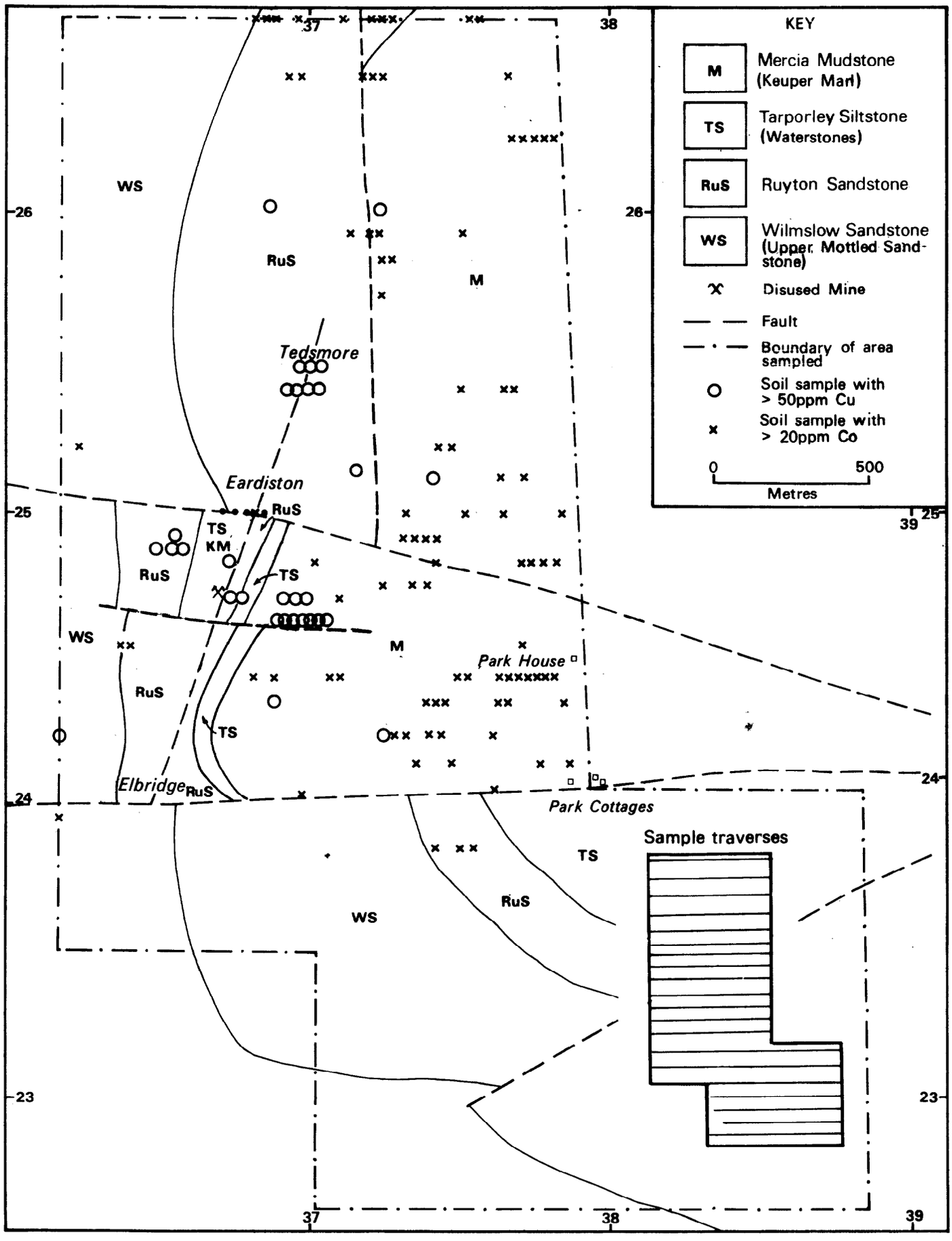

Fig. 2 Area 1: Ruyton - Eardiston

concentrated into a vein-like body. Three shafts to exploit this ore were sunk to the north of Pim Hill and a small level was driven to the vein. Little information has survived about this mine, which closed in the mid-19th century when the copper prices fell. During the 20th century trials have been conducted for cobalt but without success.

The most easterly of the faults, known as the Shotton Hall Fault, is mineralised in its northern portion where it passes to the east of Alderton. Attempts to exploit this copper ore were made in the Yorton Bank Mine from which there has survived a single shaft (now a road drainage shaft) said to be 45 m deep. There are no statistics or plans of this mining venture.

Geochemical investigation

Figure 3 depicts the locations of those samples with anomalous values for Cu, Co and Pb.

The values for these three metals as derived from the statistical treatment are as follows:

	n	$\bar{x}$	σ	Rejection limit	Range	$\bar{x} + 2\sigma$
Copper	427	24.65	12.39	90	15–190	49.43
Cobalt	427	5.65	4.66	15	0–37	14.97
Lead	427	48.11	25.6	100	5–120	99.31

There is a marked concentration of high Cu and Pb values in the area of known mineralisation at Pim Hill. The pattern produced is in accord with mineralisation existing along the fault plane, the lateral down-dip dispersal of these two elements being indicated by high values to the south-east of the summit of Pim Hill. The distribution of the high values in association with the fault may indicate that the mineralisation extends somewhat further southwards along this structure than the surface exposures or underground workings indicate.

A group of high Cu and Pb values in the area of Rabbit Hill is interpreted as being derived by dispersion from localised mineralisation along that part of the Shotton Hall Fault near to Shotton Farm and for which there is no other surface evidence.

Similar, though smaller, groups of high Pb values to the north of Godings Lane and some 700 m north-west of Harmerhill – both overlying Ruyton Sandstone – are believed to indicate minor mineralisation in the vicinity.

Anomalous Co values are much less common and as a consequence tend not to produce recognisable patterns. An exception occurs in the area to the west of Alderton and Broughton Farm where there is a concentration of high Co values, which is associated with isolated high values for Cu and Pb.

It seems unlikely that these high values are related to the known mineralisation at Yorton Bank Mine as this would mean considerable (400 m) dispersion against the general direction of ice movement (which elsewhere has had the effect of displacing soil geochemical anomalies eastwards). It is likely, therefore, that these Co anomalies and the isolated Cu and Pb in this area are related to mineralisation along an extension of the Pim Hill Fault but which does not appear to have a mappable surface expression.

AREA 3: GRINSHILL

A small area covering approximately 1.5 km^2 immediately to the south of the village of Clive was sampled (Figure 4). Soils were collected on a 100 X 100 m grid, the samples being analysed for Cu, Pb and Co. The area sampled is underlain by the Wilmslow Sandstone and by the Grinshill Sandstone and Tarporley Siltstones. The Grinshill Sandstone is the local equivalent of the Ruyton Sandstone of areas 1 and 2.

A statistical treatment of the analytical data from this area is detailed below:

	n	$\bar{x}$	σ	Rejection limit	Range	$\bar{x} + 2\sigma$
Copper	75	19.9	13.3	100	5–200	46.50
Lead	75	46.1	24.3	80	20–330	94.70
Cobalt	75	5.6	4.7	15	0–37	15

Mining interest in the area is first recorded in the 17th century, the earliest proven date of some of the old levels in the Grinshill copper mine where several shafts were sunk along the line of a north-south fault cutting the Triassic sandstones. The copper ore is found low in the Grinshill Sandstone, in areas affected by faults. The thickness of the ore is said to have varied considerably, but the average stoping width was 6 m. The carbonates of copper were accompanied by irregular 'lumps' of cobalt, barytes and iron ore, particularly on the footwall of the fault. There are no known plans or statistics of the mine but it would seem that a considerable amount of ore was removed from the known mile or so of workings believed to exist (Dewey and Eastwood, 1925).

The soil sampling grid crosses the mineralised fault and several other faults in the area (see Figure 4). Anomalous values for copper and lead show a distribution related to the position of the mineralised fault. Individual high values 500–600 m to the south may indicate sporadic mineralisation in the sandstone unit away from the old worked lode.

Anomalous Co values, unlike Cu and Pb, are isolated and scattered, as was seen in the data from Ruyton and Harmerhill, high values being obtained from the largely drift-covered area up to 800 m to the east of the mineralised vein.

Mineralisation, as indicated from the present geochemical data, appears to be restricted to the Grinshill Mine Fault.

AREA 4: WESTON

Two small areas, one north-east and the other

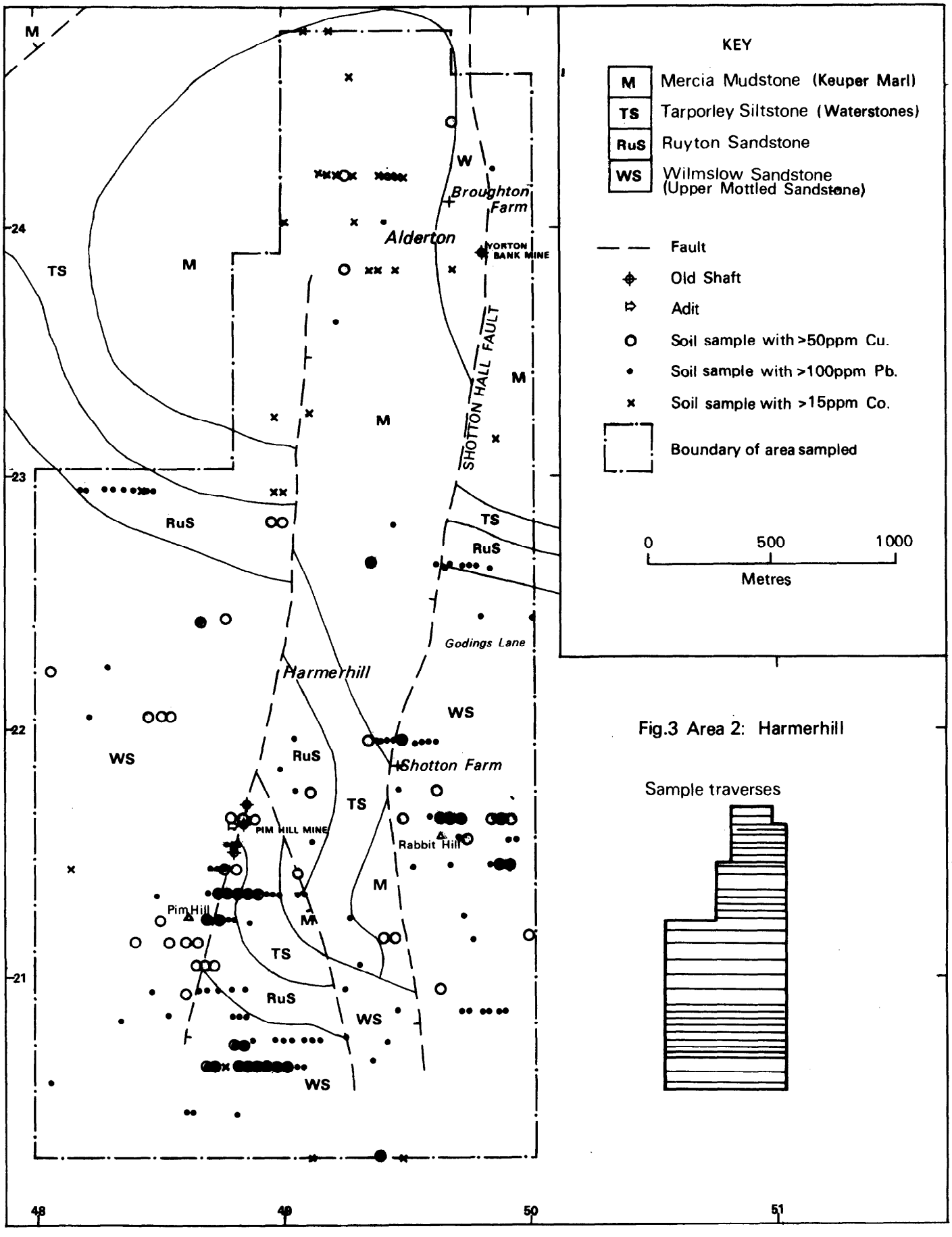

Fig.3 Area 2: Harmerhill

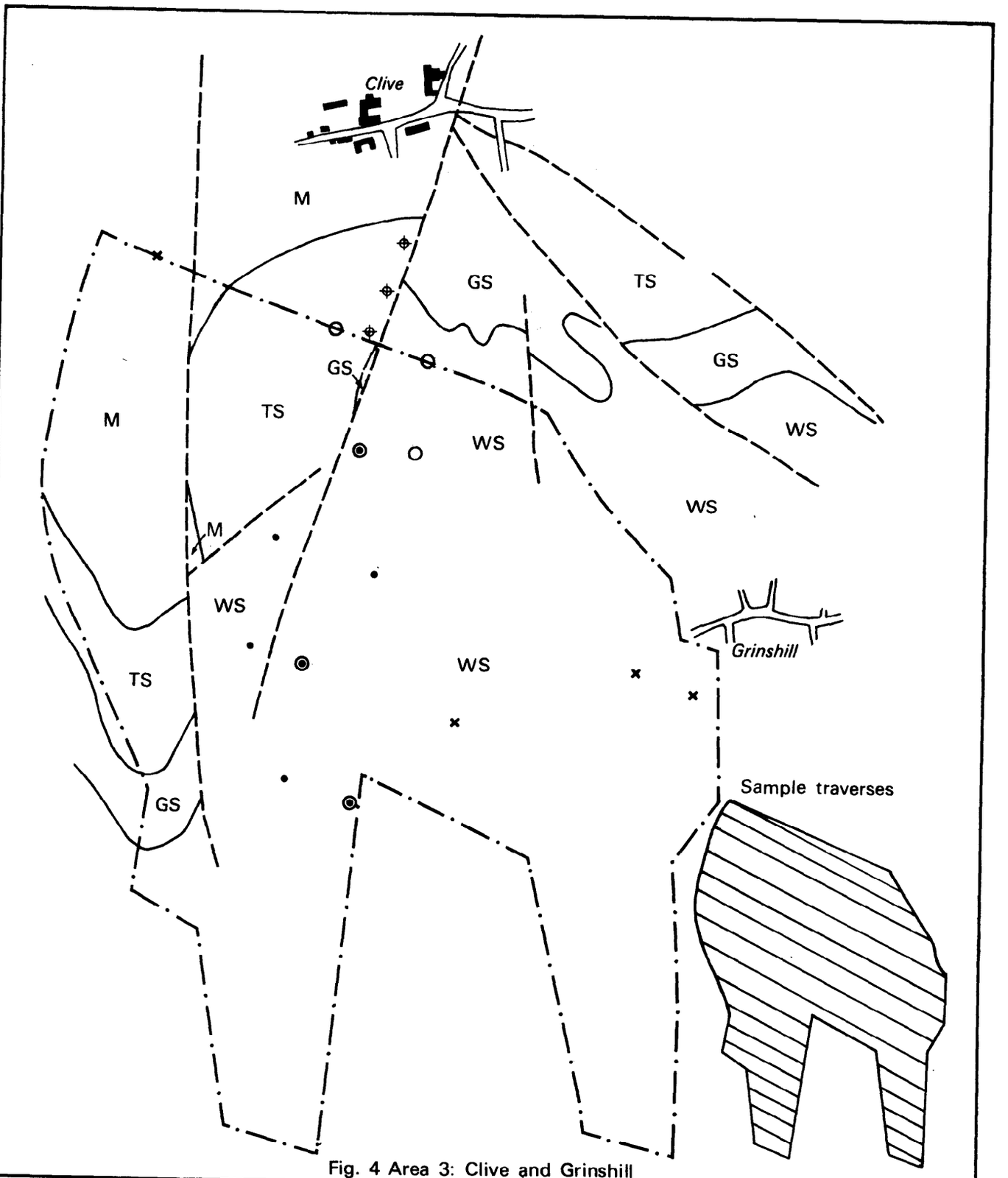

Fig. 4 Area 3: Clive and Grinshill

KEY

- Boulder Clay
- M — Mercia Mudstone (Keuper Marl)
- TS — Tarporley Siltstone (Waterstones)
- GS — Grinshill Sandstone
- WS — Wilmslow Sandstone (Upper Mottled Sandstone)
- Lithological boundary
- Fault
- Old Shaft
- Boundary of area sampled
- O Soil sample with > 45 ppm Cu.
- • Soil sample with > 60 ppm Pb.
- × Soil sample with > 15 ppm Co.

0 500 Metres

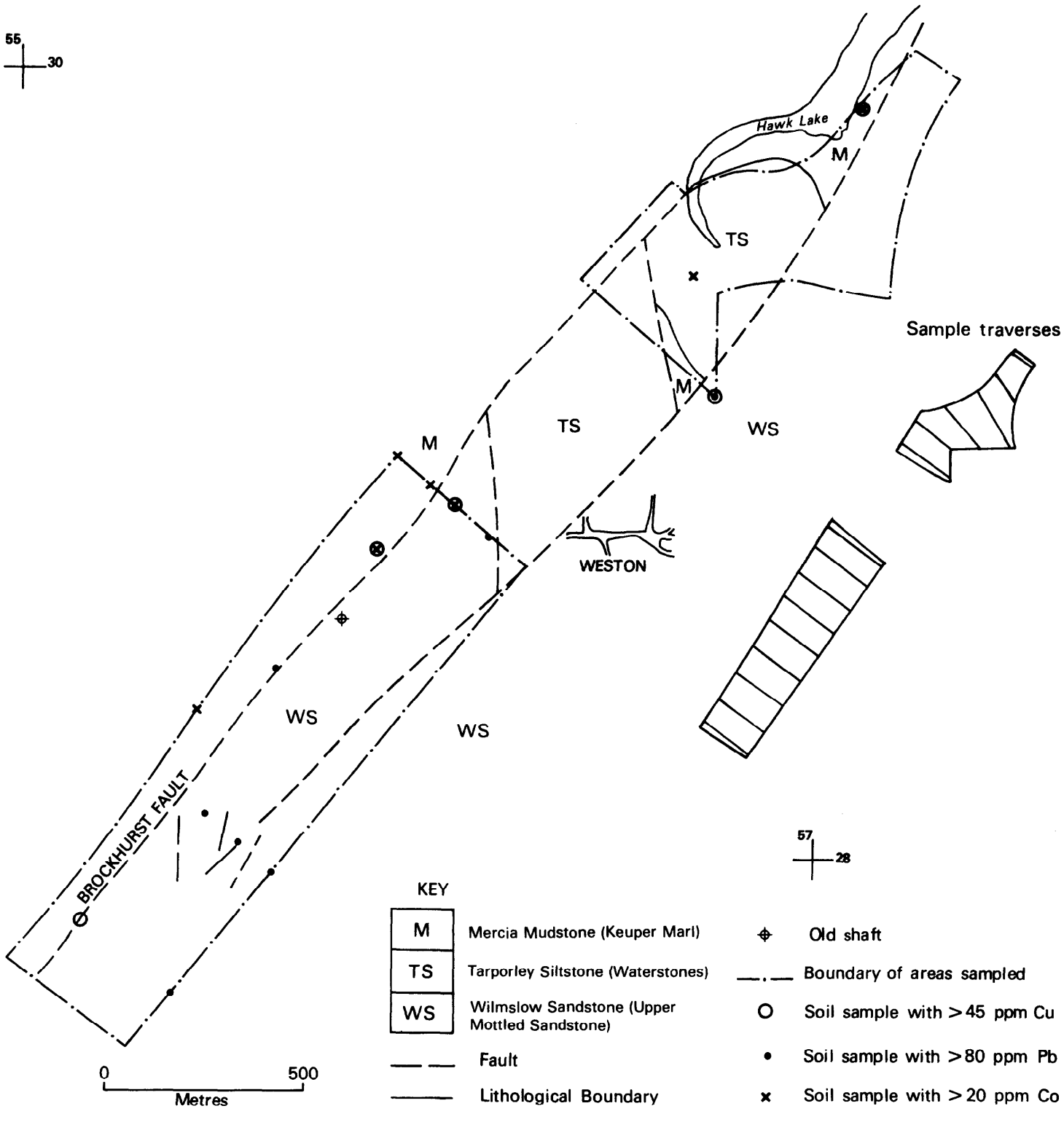

Fig.5 Area 4: Weston

south-west of the village of Weston, with a total combined area of approximately 1 km^2 were sampled on 200 X 100 m grids in order to investigate the possible extensions of the mineralisation along the Brockhurst Fault (Figure 5). The ore in this area was located along this structure where it cuts the Wilmslow Sandstone Formation (Upper Mottled Sandstone) and was worked from a shaft during the years 1865 to 1867. Copper carbonates are also found in two places along a similar parallel fault structure some 300–400 m to the east of the Brockhurst fault.

Details of the statistics of the analytical data obtained from these samples are as follows:

	n	$\bar{x}$	σ	Rejection limit	Range	$\bar{x} + 2\sigma$
Copper	69	20.7	11.5	65	10–160	43.7
Lead	69	39.6	17.3	80	10–650	74.2
Cobalt	69	10.7	4.4	20	0–20	19.5

There are only a few anomalous samples for each of these metals, but it is significant that they are closely associated with the two northeast–southwest faults. There is no marked concentration of anomalous values in the area of the old mine or in any other part of the area. It is concluded from these data that mineralisation is sparse and as in the other areas related to fault structures producing trap situations in arenaceous units.

AREA 5: ALDERLEY EDGE

This area of investigation (Figure 6) is situated approximately 19 km south of Manchester, where Alderley Edge forms an abrupt feature, rising from the drift covered plain to an altitude of 180 m. The hill consists of a faulted complex of Triassic rocks with the resistant parts of the Helsby Sandstone Formation, notably the Engine Vein Conglomerates, forming the physical features. The main mining area (Warrington, 1965; Carlon, 1979; Warrington, 1980) is bounded to east and west by the Kirkleyditch and Alderley faults respectively, with a complex of generally north-west trending faults occurring between these two major (approximately north-south) faults. Several of the faults and the more conglomeratic units of the Keuper sandstone are mineralised. The main ores are those of copper and lead but zinc, arsenic, cobalt, nickel, manganese and vanadium also are recorded.

History of mining and metal ores

The extraction of copper and lead ores may well have commenced in pre-Roman times and possibly continued during the Roman occupation. The earliest documented period of working was 1693–1698 (Warrington, 1981). Copper and lead were worked in the latter part of the 18th century and cobalt for some years after 1808. In the 20 years between 1857 and 1877 the production from West and Wood mines amounted to 250 000 tons of ore which averaged 1.25% Cu (Warrington, 1981). After this period mining declined and ceased operation in 1919 (Carlon, 1979; Warrington, 1981).

The principal copper ore is malachite which is disseminated within members of the Helsby Sandstone and concentrated along some fault planes. Azurite and chrysocolla also occur, most commonly close to faults, but they are of lesser importance. Primary sulphides (chalcopyrite, bornite, covellite and chalcocite) are rare but have been noted in restricted association with some of the major faults.

Galena and cerussite are the chief ores of lead. Both minerals occur in fault breccias and also as disseminations in the arenaceous sediments. The lead ores are reported to be associated with a baryte gangue.

The origin of the ore deposits at Alderley Edge is still the subject of much debate but the available evidence suggests an epigenetic origin (Warrington, 1980; Vaughan and Ixer, 1981).

Geochemical investigations

Samples of soil (taken from 45–60 cm depth) were collected from a grid 100 X 250 m oriented such that the traverse lines were normal to the observed strike (or presumed strike in drift areas) of the sediments. All of the samples were analysed by AAS for Cu and Pb and selected examples for Co and Ni.

In the interpretation of the soil geochemistry it was considered important to treat as separate populations those samples derived from the soils immediately overlying rock outcrops and those from soils developed on the variable but generally thick glacial deposits in the topographically lower areas. For this purpose the samples collected to the east of grid line easting 86 and south of northing line 77 (these lines roughly demarking the area of main drift) were treated as a separate population from the remaining samples. Some 784 samples represented the soil-from-rock area and 908 the soil-from-drift area.

Simple statistical treatment gave the following values for mean ($\bar{x}$) and standard deviation (σ).

	n	$\bar{x}$	σ	Rejection limit	$\bar{x} + 2\sigma$
Copper					
Soil from rock	784	77	94	380	265
Soil from drift	908	23	11	70	45
Lead					
Soil from rock	784	110	115	900	340
Soil from drift	908	57	28	190	113

There is close agreement between the anomalous areas for Pb and those for Cu. In the main they identify, as may be expected, the old mining areas around Alderley Edge and Kirkleyditch.

The anomalous copper areas (Figure 6) identify (A) the location of quite extensive dumps (now removed) of material, mined from West Mine, associated with smelting and acid leaching processing areas in use during the 19th and early 20th centuries, and at (B) an old opencast area now

infilled. The anomalies at (C) and (D) reflect the workings along the Engine Vein and at Stormy Point.

The Kirkleyditch anomaly (E) locates quite precisely the site of the process works related to the working of the Kirkleyditch Mine to the east.

There is no evidence of old workings in the vicinity of the anomalies at (F) and (G), Adders Moss and to the north of the Mount. The anomalies here are believed to indicate minor copper mineralisation associated with an extension of the mineralised fault from the main Alderley Edge mines to (F) and (G) within the conglomerate facies of the Helsby Sandstone. Small anomalies south of Danielhill and Kirkleyditch similarly are interpreted as indicating minor mineralisation along a fault and in the conglomerates of the Helsby Sandstone.

Lead anomalies occur in areas A, B, C and D and similarly reflect the old mining activity although these anomalies tend to be more extensive. Interestingly, the eastward extension of anomaly (A) includes the Wood Mine which gives no comparable Cu anomaly.

The Cu anomalies at Adders Moss, The Mount and Kirkleyditch (F, G, E) are not accompanied by overlapping high lead areas. High anomalies south and west of Adders Moss cannot be explained in terms of identifiable mining operations and are probably reflections of mineralisation in the conglomerates and sandstones of the Helsby Sandstone Formation. The orientation of this anomaly in an area of poor natural exposure may indicate either mineralisation of an unknown fault structure or that the strike of the lithological units accompanied by some mineralisation, is slightly different from that inferred on published maps.

The anomaly at Kirkleyditch (with values of 1400 ppm Cu and 5000 ppm Pb) is not closed to the north, and although these high values undoubtedly represent contamination from old mine dumps further sampling should be undertaken northwards from this area to determine the geographical extent of the geochemical feature. There are several isolated anomalous samples scattered throughout the area, but they do not present a coherent pattern that can be reliably interpreted.

CONCLUSIONS

The investigations so far conducted have been confined to those parts of the Triassic outcrop where there is some history of known mineralisation and mining. In four of the five areas there is some cover of glacial till which masks to some extent the underlying solid geology. At Alderley Edge there is an area which is almost entirely free of drift, as a consequence of which the analytical data have been divided into two different populations, one related to the soils derived from bedrock and the other to areas of extensive drift.

The threshold values for each of the elements studied in each area is given below:

Area	Cu	Pb	Co	
1	50	60	20	
2	50	100	15	
3	45	95	20	
4	45	75	20	
5	45	115	—	drift-derived soil
	265	340	—	rock-derived soil

The threshold values over drift-covered ground are similar in all five areas, but the thresholds for copper and lead are substantially higher in the drift-free Alderley Edge, illustrating the dilution effect of extensive glacial till cover.

The data from the five areas indicate a commonly occurring connection between mineralisation, faulting and suitable host lithologies in the sediments. Mineral concentrations are recorded from both fault zones and from suitably porous host rocks.

The physical association of mineralisation with fault planes, however, does not necessarily mean that the mineralising fluids came up from depth along them. There is adequate information from the area to suggest that the importance of the faults lies in their role in the formation of stratigraphic traps which effectively prevented the further lateral migration of metal-containing fluids through porous sandstone and conglomerate (Alderley Edge) units.

The applicability of normal geochemical soil sampling techniques is seen to be of value in the areas covered by relatively thin drift adjacent to known mineralisation, but it has not yet been applied to areas where potential, favourable host rocks may lie totally unexposed beneath thick cover.

ACKNOWLEDGEMENTS

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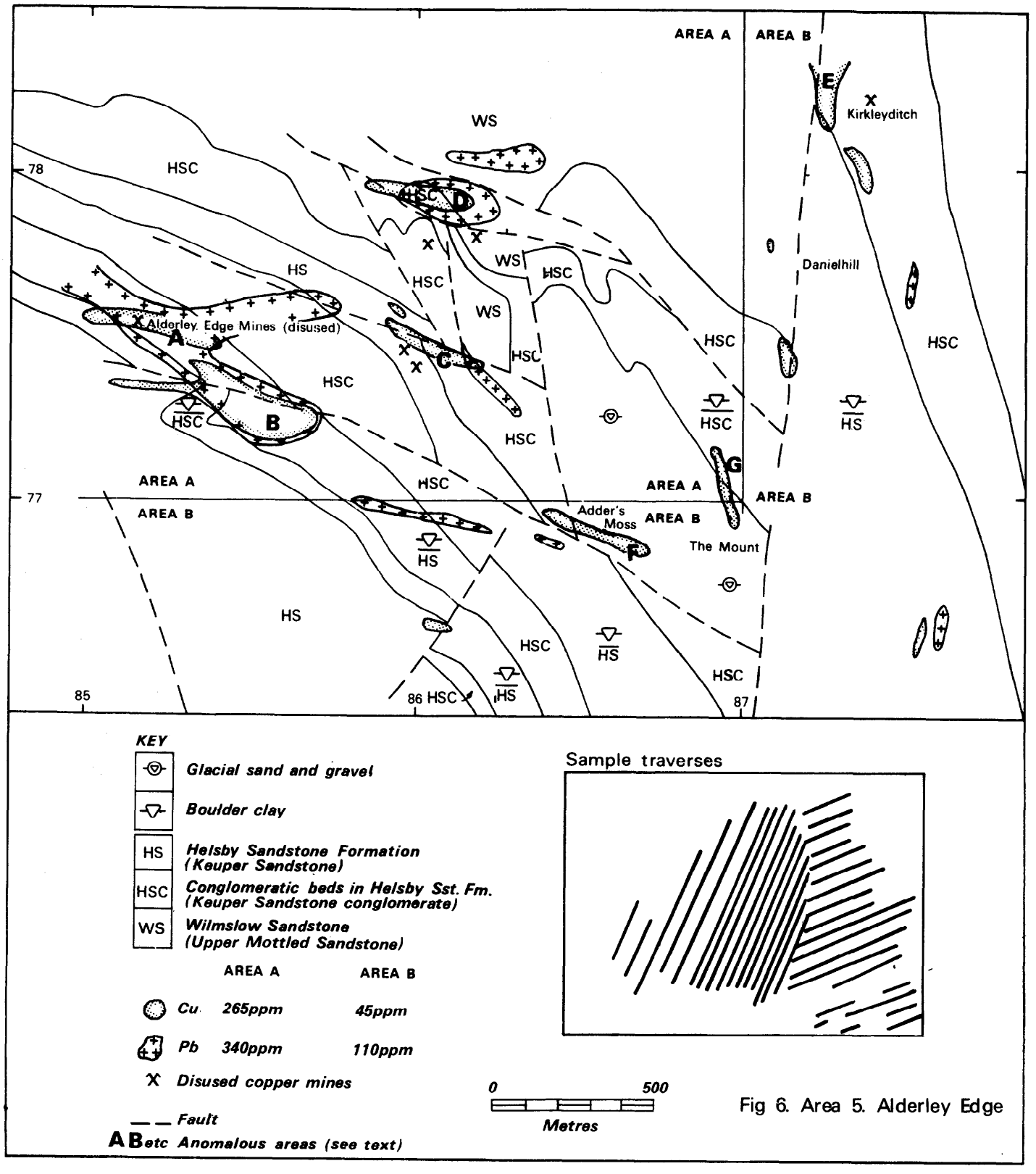

Fig 6. Area 5. Alderley Edge

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INSTITUTE OF GEOLOGICAL SCIENCES

Natural Environment Research Council

Mineral Reconnaissance Programme

Report No. 52

Titanium dioxide in the Ayrshire Bauxitic Clay

I. B. Cameron

CONTENTS

FIGURES

Bibliographic reference
Cameron, I. B. 1982 Titanium dioxide in the Ayrshire Bauxitic Clay *in* Miscellaneous investigations on mineralisation in sedimentary rocks *Mineral Reconnaissance Programme Rep. Inst. Geol. Sci.*, No. 52, pp. 14–18

London 1982

A report prepared for the Department of Industry

INTRODUCTION

The Ayrshire Bauxitic Clay is a rather variable bed of indurated clayrock resting on top of the Passage Group lavas of the Carboniferous in north Ayrshire. It consists mainly of kaolinite, with the bauxitic minerals diaspore and boehmite present in places. The outcrop extends from the coast at Saltcoats eastwards to the Fenwick Water, north of Kilmarnock, a distance of about 24 km. The clay also occurs in faulted outliers to the north of the main outcrop (Figure 1). The deposit has been described by Wilson (1922) and it is categorised as belonging to the kaolinite clayrock facies by Loughnan (1978).

The seam varies in thickness from a few centimetres to about 9 m. It averages about 1.5 m in the main outcrop, but it is thicker in the outliers to the north of the Dusk Water Fault. Little is known of the thickness or extent of the clay to the south of the main outcrop, where it is overlain by Coal Measures.

The clay is believed to be the product of prolonged contemporaneous weathering of the underlying Passage Group lavas, under warm humid conditions. The lavas are olivine basalts, mainly of Dalmeny type, the top surface of which has been lateritised and bauxitised.

The Bauxitic Clay may be, in places, detritus from the lavas which have been weathered and altered *in situ*. Elsewhere there is evidence of sedimentary re-working and in places ooliths and pisoliths have been formed.

The Bauxitic Clay has been worked since the First World War as a refractory and as a source of alum. Most extraction has been from small opencast pits, but there has also been some underground mining. At the present time there are two small opencast pits in operation, one owned by Laporte Industries and the other by A. P. Green Refractories Ltd.

TiO_2 CONTENT

There are several published analyses of the Ayrshire Bauxitic Clay (Wilson, 1922) and many more exist in company files and in IGS records. A total of about 223 partial analyses are available and the arithmetic mean of the percentage TiO_2 in these samples was found to be 4.68%. The range of values was from 1.2% to 14.17% but only nine samples exceeded 10%. The Interquartile Range is 2.39%, which means that 50% of the values for TiO_2 fall within the range from 3.33% to 5.72%.

A histogram of the distribution is shown in Figure 2.

SOURCE OF THE TiO_2

The obvious source of the TiO_2 in the Ayrshire Bauxitic clay is the Passage Group lavas from which the clay is derived. The TiO_2 occurs in the resistate minerals, rutile, titanomagnetite or ilmenite, and it tends to become relatively concentrated in residual deposits. The concentration of TiO_2 tends to parallel the enrichment in Al_2O_3.

Macdonald and others (1977) give eight analyses of Passage Group lavas. The average TiO_2 content for the eight samples is 2.19%. The average Al_2O_3 content is 14.77%. If weathering processes on these basalts led to a residual deposit with an Al_2O_3 value equal to that of the Bauxitic Clay (average 37.31%) then the level of TiO_2 which one might expect in such a residual deposit is 5.53%.

It is reasonable to assume that the average TiO_2 values found in the Ayrshire Bauxitic Clay can be explained by a simple process of residual concentration. The very few higher TiO_2 values may be due to local re-working of the residual deposit with the localised formation of titanium-bearing heavy mineral placers, or to migration in solution and redeposition, probably as anatase.

OUTLINE OF TITANIUM ORE PRODUCTION

The countries with the largest production of TiO_2 are Australia, Canada, Norway and Malaysia. The principal sources of the mineral are placer deposits of rutile and ilmenite (from Australia, Malaysia and India), and primary deposits of ilmenite and titaniferous magnetite in gabbros and anorthosites (in Canada and Norway).

Most of the TiO_2 production is used as the dioxide in paint and plastics as a pigment. Only 3–4% is used to make titanium metal.

Relatively high concentrations of TiO_2 occur in bauxites. The maximum is about 30% but figures between 10% and 15% are common. Bauxite is not currently an economic source of titanium. In spite of a considerable volume of research on the recovery of titanium from bauxite, its extraction has not yet proved to be profitable.

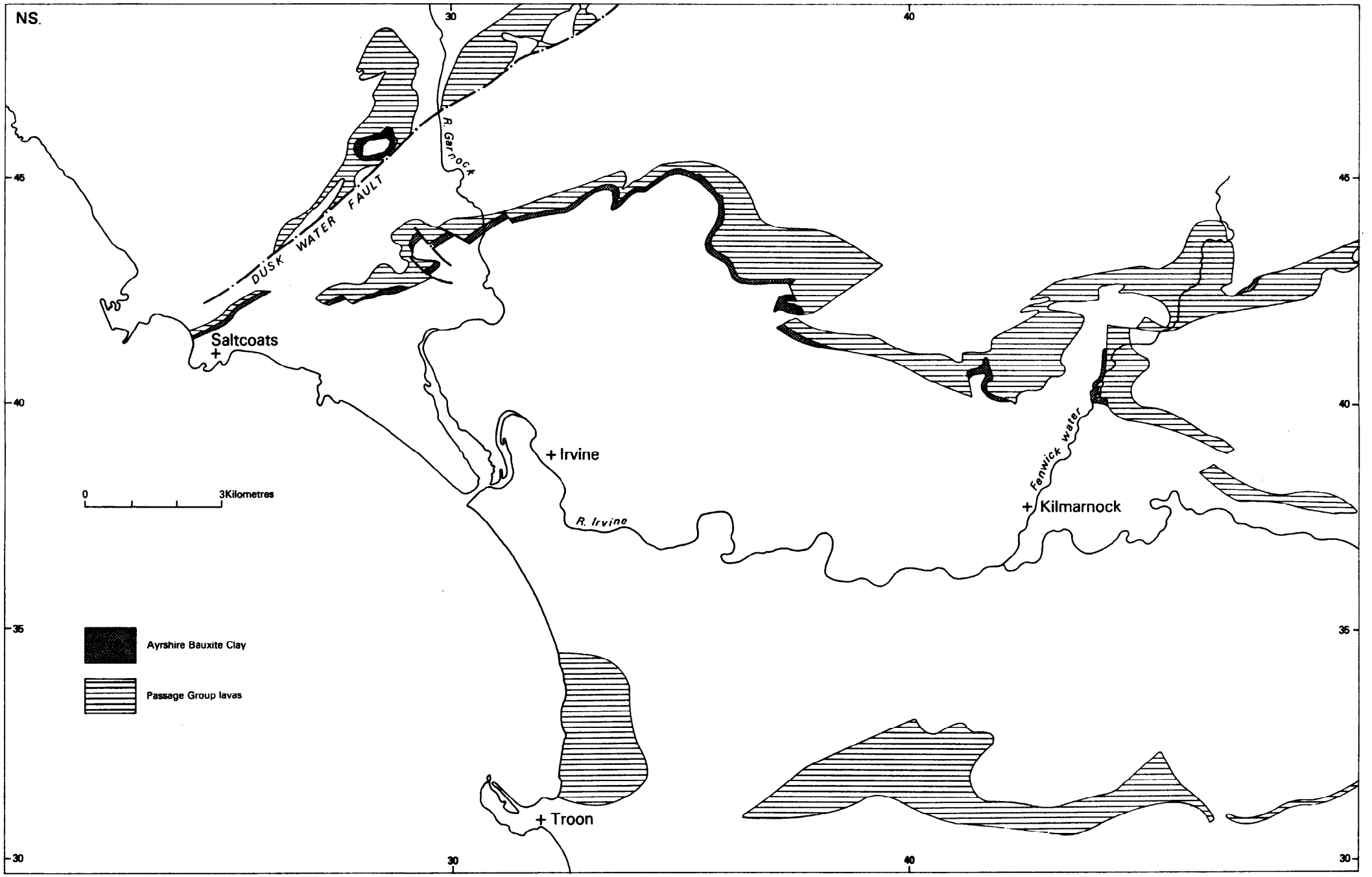

Fig. 1: Outcrop Map of the Ayrshire Bauxitic Clay

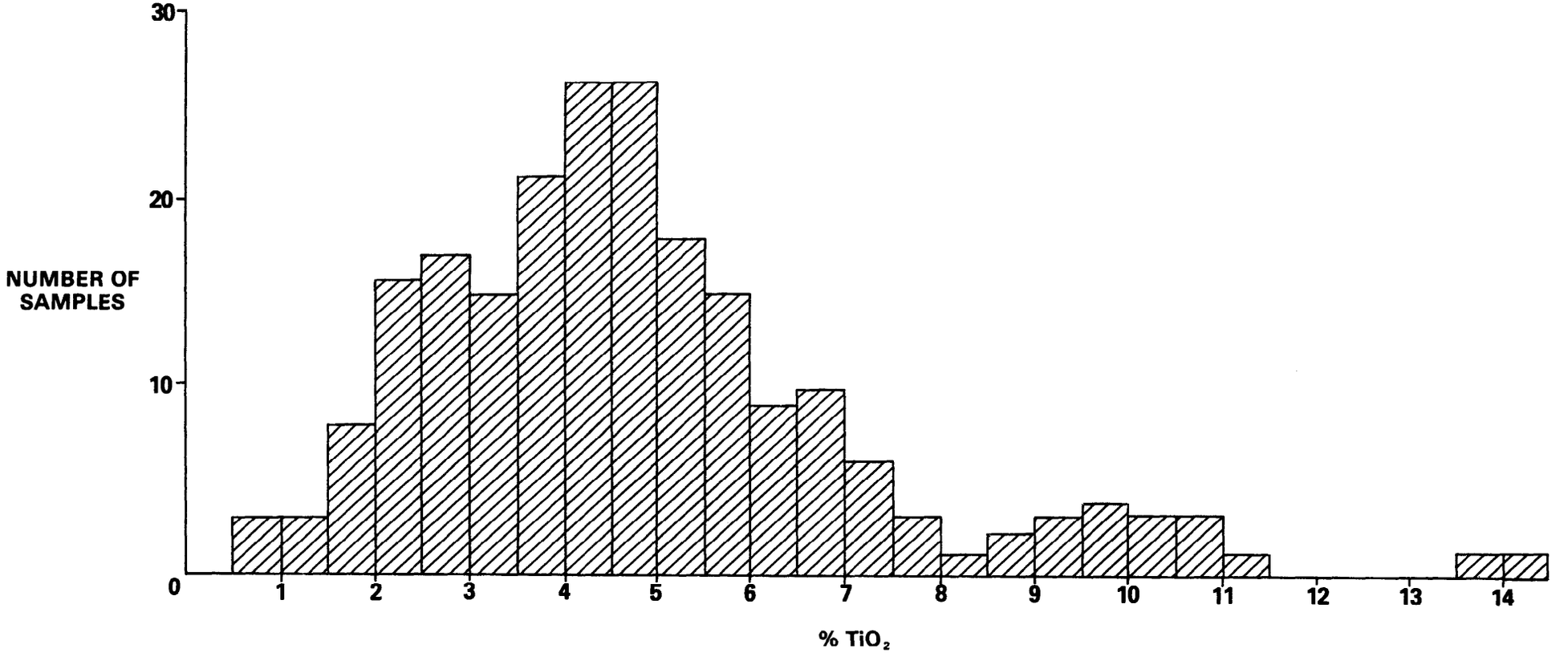

Figure 2. Histogram of the distribution of TiO_2 percentages in analyses of the Ayrshire Bauxitic Clay

CONCLUSION

The average TiO_2 content of the Ayrshire Bauxitic Clay is less than 5%. The deposit is thin, widespread and already partially worked both opencast and underground. The titanium mineral is very finely divided and, as yet, there is no profitable way of extracting it from bauxitic rocks, even at much higher grades.

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Natural Environment Research Council

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Report No. 52

The Marl Slate (Kupferschiefer) in the Southern North Sea Basin

H. W. Haslam

CONTENTS

Bibliographical reference
Haslam, H. W. 1982 The Marl Slate (Kupferschiefer) in the Southern North Sea Basin *in* Miscellaneous investigations on mineralisation in sedimentary rocks. *Mineral Reconnaissance Programme Rep. Inst. Geol. Sci.*, No. 52, pp.19–26

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INTRODUCTION

The Marl Slate of north-east England and its equivalent in Germany and Poland, the Kupferschiefer, are rich in Cu, Pb, Zn and other metals, although in England the concentrations of these elements do not reach economic levels (Deans, 1950; Hirst and Dunham, 1963). The existence of the Marl Slate under the North Sea has been noted (e.g. Blanche, 1973, 1974), but no data have been made available hitherto on the metal contents.

In this investigation, borehole material was obtained from nine wells which intersected the Permian in the UK sector of the Southern North Sea Basin (Figure 1). The samples were analysed by Mather Research Limited for a range of elements known to be concentrated in this lithology (Tables 1 and 2), using the atomic absorption method.

RESULTS

Well 41/18-1 The Kupferschiefer had been recorded at 5290–5292 ft. Three core samples were collected from the formation, sample 46 from 5289 ft, 47 from 5291 ft and 48 from the base, at 5292 ft. Sample 48 contains a few percent of pyrite, but 47 is the blackest and most bituminous. The latter sample contains 340 ppm Cu and 120 ppm As, but otherwise the composition is unremarkable (Table 1).

Well 41/25A-1 The Kupferschiefer had been recorded at 5650–5654 ft. The core samples 49 (5650 ft) and 50 (5652 ft) are hard grey mudstones, and 51 (from the base of the Kupferschiefer at 5654 ft) is black and carbonaceous. Sample 51 contains high levels of Cu, Pb, Zn, V, Mo, Ni, Co and As.

Well 43/3-1 The Kupferschiefer has been recorded with a thickness of about 6 ft at a depth of about 9720 ft. This section of the well was not cored, but chippings were retained. Samples 1–40 are samples of chippings, from 10 ft or 5 ft lengths, between 9700 and 10035 ft. Samples 1–7 (9700–9775 ft) appear from the chemical analyses (Table 2) to contain some material derived from the Kupferschiefer, the highest metal values being recorded in sample 3 (9720–9730 ft), with 62 ppm Cu, 300 ppm Pb, 2300 ppm Zn, 370 ppm V and 110 ppm Mo. Below 9730 ft, the borehole passes through Lower Permian and probably Upper Carboniferous strata and, except for 110–115 ppm Pb in samples 32–35 (9930–9975 ft), no enhanced metal levels are recorded.

Well 44/11-1 The Kupferschiefer had been recorded at 11159–11163 ft. Samples 41 (11159 ft), 42 (11160 ft), 43 (11161 ft), 44 (11163 ft) and 45 (11163–4 ft) are fine-grained grey sediments, 42 being the darkest. Sample 42 has the highest values of Cu (200 ppm), Pb (250 ppm), V (1400 ppm), Ni (250 ppm), As (120 ppm) and Mo (350 ppm), but, unlike samples from other wells, Zn values are higher than Cu and the highest Zn content (1.3%) is in sample 41.

Well 44/21-1 The Kupferschiefer had been recorded at 12671–12674 ft, but no sign of it was found in the core, and a sample from that depth (sample 52) has a Zechstein lithology and shows no exceptional metal contents.

Well 48/6-1 The Kupferschiefer had been recorded at 8701–8703 ft, but it was found in the core at a slightly higher level. Sample 53 is a hard grey mudstone from the base of the formation, at 8699 ft 6 inches, and has slightly enhanced values of Pb, V, Ni, Co and As. Samples 54 and 55 come from grey shaly bands in the underlying Rotliegendes, at 9520 and 9643 ft respectively, but the metal contents are not worthy of note.

Well 48/12-2 Sample 59 is a fine-grained grey sediment, which appears to represent the upper part of the Kupferschiefer; it shows no interesting metal values. Sample 60 is a darker mudstone at the base of the Kupferschiefer, which is approximately 1 ft thick. It has a high Cu content (7000 ppm), accompanied by enhanced Pb, V, Ni, Co, As and Mo values. Sample 61 is a dark grey sandstone from 2 inches below the base of the Kupferschiefer. Some green staining is apparent, and the rock contains anomalous levels of Cu (1200 ppm), Pb (210 ppm), Zn (460 ppm), Co (340 ppm) and As (332 ppm), though values for V, Ni and Mo are low.

Well 49/20-1 The Kupferschiefer had been recorded at 7905–7906 ft. Examination of the core showed it to be 3 inches in thickness, at

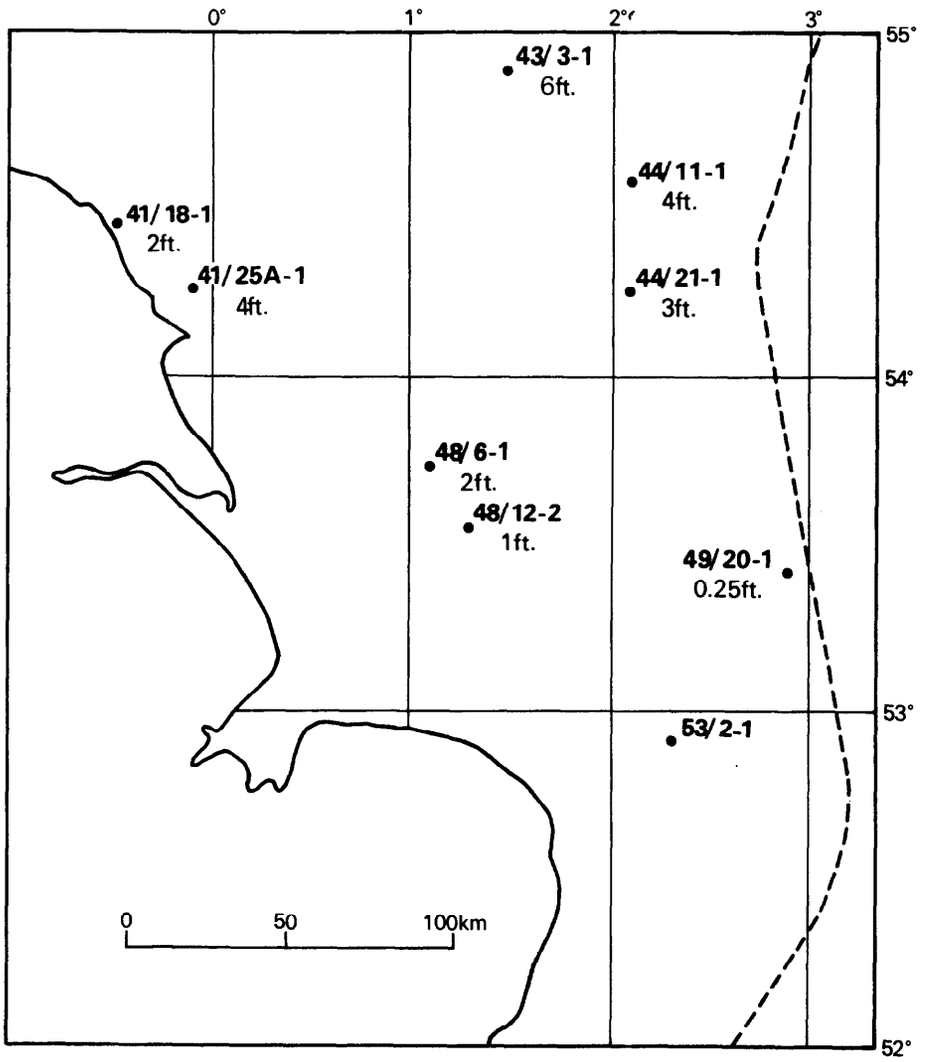

Fig. 1: Approximate localities of the boreholes from which samples were taken, with the thickness of the Kupferschiefer formation.

Table 1 Geochemical data for core samples

Sample No.	*Cu*	*Pb*	*Zn*	*Ag*	*V*	*Ni*	*Co*	*Sb*	*As*	*Cr%*	*Mo†*	*Sn*	*Mn*
41	100	80	13000	x	150	84	24	5	15	0.01	30	20	1200
42	200	250	1700	x	1400	250	46	7	120	0.05	350	8	600
43	44	80	1300	x	150	70	24	3	17	0.01	20	12	1100
44	28	55	60	x	80	52	20	2	9	0.02	20	16	1450
45	32	55	34	x	50	58	24	4	10	0.01	10	x	1100
46	38	85	28	1	90	80	28	5	24	0.03	20	x	1250
47	340	75	56	x	80	88	60	7	120	0.02	20	x	650
48	44	60	44	1	80	88	54	5	24	0.02	20	x	340
49	58	55	30	x	70	50	22	2	5	0.01	20	x	700
50	28	60	28	x	60	60	20	3	6	0.01	20	x	1450
51	750	340	116	2	1650	310	230	5	176	0.01	300	x	800
52	16	25	200	x	30	12	8	2	5	0.03	10	12	60
53	92	130	52	2	160	116	160	5	136	0.01	20	x	420
54	34	25	18	x	80	40	18	6	14	0.02	10	x	600
55	28	45	58	x	60	48	24	5	8	0.03	10	x	900
56	3000	125	38	6	1500	380	570	7	120	0.02	400	16	570
57	100	85	64	1	300	180	180	6	142	0.03	80	x	450
58	78	85	68	2	360	180	170	4	148	0.01	50	24	400
59	84	45	20	1	50	36	32	2	14	0.03	10	8	1650
60	7000	170	58	4	1300	310	460	9	214	0.02	250	8	330
61	1200	210	460	1	60	82	340	5	332	0.08	30	36	300

x Below limit of detection
† Semi-quantitative
All results in ppm unless otherwise stated.

Table 2 Geochemical data for chippings samples

Sample No.	*Cu*	*Pb*	*Zn*	*V*	*Mo* †
1	52	80	590	40	20
2	32	60	240	40	20
3	62	300	2300	370	110
4	50	175	1500	180	50
5	36	95	1000	80	30
6	32	75	470	70	30
7	34	80	480	80	30
8	24	90	280	40	20
9	24	90	280	40	20
10	32	75	170	50	10
11	32	85	170	60	10
12	30	60	116	60	10
13	32	65	116	70	10
14	36	55	108	60	10
15	36	55	110	50	20
16	40	85	104	60	10
17	38	50	112	70	10
18	24	85	200	70	10
19	26	85	200	70	10
20	32	70	120	60	10
21	30	65	110	60	10
22	64	50	130	60	10
23	64	50	130	70	10
24	30	45	96	60	10
25	32	50	96	60	10
26	32	55	108	50	10
27	34	50	108	50	10
28	32	50	100	60	10
29	34	50	96	60	10
30	42	55	82	60	10
31	46	55	84	60	10
32	36	110	96	70	10
33	36	115	100	70	10
34	38	115	180	70	10
35	40	115	180	60	10
36	40	50	80	60	10
37	38	45	80	50	x
38	34	50	82	60	x
39	34	55	98	50	x
40	34	50	80	60	x

x Below limit of detection
† Semi-quantitative
All results in ppm.

7908 ft. It is a black, carbonaceous rock (sample 56), with 3000 ppm Cu, 125 ppm Pb, 1500 ppm V, 380 ppm Ni, 570 ppm Co, 120 ppm As and 400 ppm Mo.

Well 53/2-1 A shale band had been recorded at the base of the Upper Permian, at 6254–6294 ft, and the lower part of this is regarded as Kupferschiefer. Two samples were collected. Sample 57, a dark shale from 6291 ft, and sample 58, from the base of the dark shale at 6294 ft. Both samples contain slightly enhanced levels of Cu, Pb, V, Ni, Co, As and Mo, so it is probable that they represent part of the Kupferschiefer.

DISCUSSION

In most of the wells, the recorded thickness of the Kupferschiefer is in the range 1–6 ft (Figure 1), but in one core, 49/20-1, the formation was observed to be merely 3 inches thick. Records of 33 other wells in the Southern North Sea Basin show the thickness to be generally 1–6 ft.

As a check on the analytical results obtained by the atomic absorption method, three samples were scanned by XRF, 41, 56 and 60. Agreement for Cu, Pb, Zn, Ni, Co and As was good, but agreement for Mo was less good. Semi-quantitative XRF determinations gave 690 ppm Mo for sample 56 and 470 ppm Mo for 60, compared with 400 and 250 ppm by AAS. There is therefore the possibility that the above-background Mo results should be increased by about 80%. The close correlation between Mo and V suggests that, if there is an error in the AAS results for Mo, it is a systematic one, and Fe suppression is a more likely cause than incomplete digestion under perchloric acid attack. The higher levels for Mo obtained by XRF are more in agreement with the Mo:Ni ratios obtained in north-east England by Hirst and Dunham (1963) (using XRF), but the lower (AAS) levels are more consistent with the Mo:Ni and Mo:V ratios obtained on the samples from the Continent by Wedepohl (1964) using optical emission spectrography.

In five wells, a sample collected from the base of the Kupferschiefer may be compared with one or more samples from higher in the formation. In 41/25A-1 and 48/12-1, the highest metal contents are in the basal sample; in 41/18-1 and 44/11-1 the highest values are higher in the succession, and in 53/2-1 the two samples are similar in composition. In the first four of these boreholes, there are very considerable differences in metal content between samples taken from different levels within the Kupferschiefer.

The great variability both within and between boreholes means that no precise generalised statements can be made about the levels of metals in the Kupferschiefer under the North Sea, but some observations may be made from an examination of the data and comparisons with other areas.

In the Marl Slate in Durham, Hirst and Dunham (1963) found that Mo, Co and Ni were all correlated with organic carbon, and the same applied to Cu, to some degree. In the Kupferschiefer of north-west Germany, Wedepohl (1964, 1971) found that V, Cr and Ni were related to the carbon content, and probably also Mo and Co.

In the North Sea samples, the carbon content was not determined, but samples 42, 47, 51, 53, 56, 57 and 58 may be described as black shales and most of them are enriched in Cu, Pb, V, Ni, Co, As and Mo. To this list may be added samples 3 and 60, which are enriched in some of the same suite of elements: sample 3 was not described, because there was no core, while sample 60 is a dark mudstone, lacking the sooty appearance and fine lamination of the black shales. These nine samples (from eight wells) are plotted on Figure 2. V and Mo correlate closely, and V was chosen to plot the other elements against. Ni correlates well with V. Co correlates well except for two samples. These four elements are all low in the nine Kupferschiefer samples which are not classed as black shales and not plotted in Figure 2. As is not related so closely to V, but there is a clear threshold between the black shales (120 ppm or above) and the other Kupferschiefer samples (24 ppm or below). Cu and Pb do not correlate well with V, though the black shales normally contain more of these elements than the other Kupferschiefer samples. Zn is low in most of the black shales, and does not correlate closely with V. It is very much higher in sample 41 than in any of the black shales. V, Ni, Mo and Co thus appear to have organic affinities, but Cu, Pb, Zn and As do not.

Of the 17 samples of Kupferschiefer, 12 contain 100 ppm Cu or less. In this the results compare with those from south-east Durham (Hirst and Dunham, 1963), where the Cu values are generally low. In the two most condensed sections, however, Cu contents of 3000 ppm (49/20-1) and 7000 ppm (48/12-2) were found, considerably in excess of the highest value recorded in Durham (754 ppm). The Southern North Sea Basin thus appears to be transitional between the low Cu of north-east England and the high Cu of Germany.

Pb values range from 45 to 340 ppm, and are generally lower than in Durham and much lower than in Germany. Zn is mostly in the range 20–116 ppm, similar to Durham, but, as in Durham, there is one section of core with a very high zinc content (up to 13000 ppm in 44/11-1). Another borehole from the north-west of the Basin, 43/3-1, also shows high Zn values, with up to 2300 ppm Zn in chippings.

Contents of Ag and Sb are low, but they tend to be slightly higher in the black shales. Cr is low

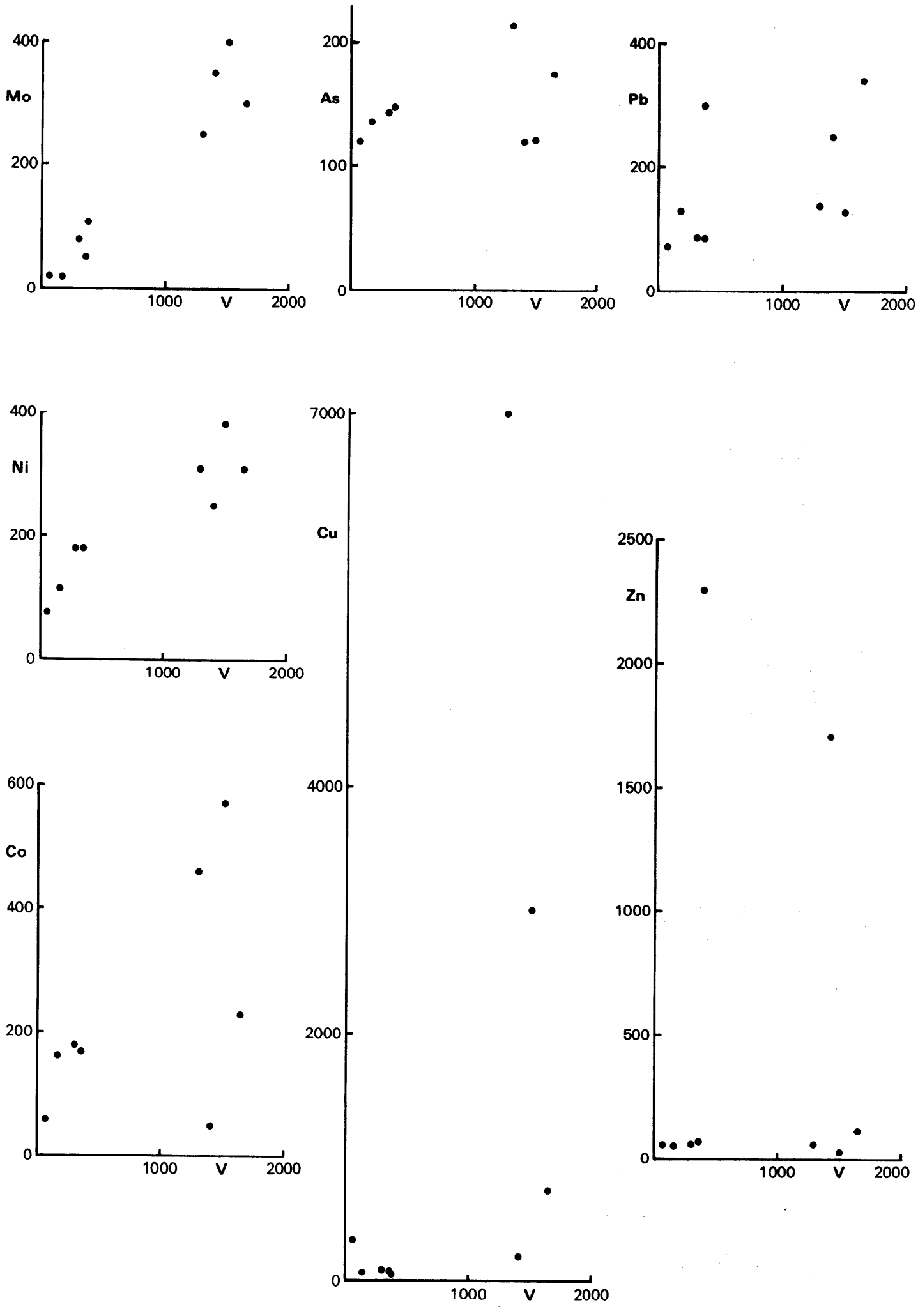

Fig. 2: V, Mo , Ni, Co, As, Cu, Pb and Zn contents of black shales.

and shows little variation. Mn is generally lower in the black shales than in the other Kupferschiefer specimens. Sn shows no pattern.

Sample 61, from just below the Kupferschiefer, contains low V, Ni and Mo, and probably has little or no organic matter, but Cu, Pb, Zn, Co and As are high. It seems likely that these concentrations were derived by leaching of the overlying Kupferschiefer.

In conclusion, the Kupferschiefer under the Southern North Sea Basin shows similar geochemical characteristics to these described from Germany and north-east England. Two samples contained high levels of Cu (3000 and 7000 ppm) and one contained high Zn (1.3%). The Pb contents are low (maximum 340 ppm).

ACKNOWLEDGEMENTS

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